TETRACHLORDINITROETHANE[1]

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Tetrachlordinitroethane is a white, crystalline solid, insoluble in water, soluble in alcohol, ether, and ligroin. In ether and ligroin it decomposes at 60° with evolution of brown fumes. It is also very soluble in liquid N_2O_4 and somewhat less so in carbon tetrachloride. When pure, decomposition does not begin until the compound is heated about to its melting point, 142–143°. It is probable, though not proved that the behavior in ligroin is due to a difference in reaction velocity rather than to a difference in equilibrium. Tetrachlordinitroethane is toxic to mice at one-sixth the concentration for chlorpicrin. It produces lachrymation in man at one-eighth the concentration that chlorpicrin does. It is not stable when exploded in a three-inch shell, but would probably stand up satisfactorily if dissolved in chlorpicrin.

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The only method of preparation described in the literature is that of Kolbe[2] who heated a mixture of nitrogen peroxide and tetrachlorethylene in a sealed tube at 110°–120° for three hours. The tube was opened, the excess N_2O_4 allowed to boil away, and the crystals of $C_2Cl_4(NO_2)_2$ collected and analyzed. Biltz[3] obtained a larger yield by heating for the same length of time to 100°–110°. We have obtained the best results at about 80°; but, even at this lower temperature, the pressure developed in the tube is apt to cause a violent explosion except when tubes of very small cross-section are used. The danger of explosion increases very much if the nitrogen peroxide is not dried by distillation over phosphorus pentoxide, as an oxidation takes place when moisture is present, giving rise to a high pressure even when the tubes are cooled in ice before being opened.

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[1] Published by permission of the Director of the Chemical Warfare Service.

[2] Ber. deutsch. chem. Ges., **2**, 326 (1869).

[3] Ibid., **35**, 1528 (1902).

Quantitative Study of the Reaction

The nitrogen peroxide was obtained by heating lead nitrate in a long, glass tube at about 400°, drying the evolved gases with P_2O_5, and liquefying the nitrogen peroxide by means of ice and hydrochloric acid. Liquid nitrogen peroxide was also prepared by the interaction of arsenic trioxide and nitric acid, and was furnished to us by the small Scale Manufacturing Section; but this had to be dried over phosphorus pentoxide before it would give satisfactory results. The tetrachlorethylene was obtained by cracking carbon tetrachloride.

Six small tubes of about 2 cc capacity were made by fusing ordinary 4 mm soda-glass tubing. Into each was introduced known weights of N_2O_4 and C_2Cl_4, so that three contained an excess of the former, and three an excess of the latter. In each case the volume of the liquid was approximately $^2/_3$ of the capacity of the tube.

The tubes were divided into pairs, and heated in the water bath. The conditions and results of the experiment are summarized in Table I.

TABLE I

	Temp. °C	Time of heating	Yield		Yield
			Theory	Obs.	
(1) N_2O_4 excess	60°	3 hrs.	0.867 g	0.311 g	35.9%
(2) C_2Cl_4 excess	60°	3 hrs.	1.472 g	0.317 g	21.4%
(3) N_2O_4 excess	60°	6 hrs.	1.085 g	0.486 g	44.8%
(4) C_2Cl_4 excess	60°	6 hrs.	1.563 g	0.524 g	33.5%
(5) N_2O_4 excess	80°	3 hrs.	0.716 g	0.570 g	79.5%
(6) C_2Cl_4 excess	80°	3 hrs.	1.152 g	0.758 g	65.8%

In every case a considerable pressure was observed on opening the tubes.

Since the production of tetrachlordinitroethane involves merely the addition of N_2O_4 to C_2Cl_4 and the opening of the double bond as follows:

$$Cl_2C = CCl_2 + N_2O_4 \longrightarrow \begin{matrix} Cl_2C - CCl_2 \\ NO_2 \quad NO_2 \end{matrix}$$

it is logical to assume that a diminution of pressure should result in the tube as the reaction progresses. This, as we discovered, was not the case. Nitrogen tetroxide is intermediate in composition between nitrous and nitric anhydride and reacts as follows with cold water:

$$O_2N - NO_2 + HOH \longrightarrow H_2NO_2 + HNO_3$$

If the water is heated, however, the unstable nitrous acid breaks down, giving nitric acid and nitric oxide.

$$3N_2O_4 + 2HOH \xrightarrow[\text{(heated)}]{} 4HNO_3 + 2NO\ ,$$

Thus the presence of hot water vapor in the reaction mixture will produce HNO_3 and NO; and an oxidation of C_2Cl_4 with the production of phosgene becomes possible. This would account for the pressure developed.

Four tubes were prepared from 4 mm tubing, and the open ends drawn to a capillary, bent in the form of a U, so that any gas resulting from the heating could be collected over mercury. One cc of a mixture of equal volumes of N_2O and C_2Cl_4 was introduced into each. Two were carefully kept dry, but two were allowed to absorb moisture until the contents became blue when frozen. The conditions of the experiments and results are summarized in Table II.

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TABLE II

	Temp.	Time	Volume of gas evolved
(1) Contents moist	60°	3 hrs.	35 cc
(2) Contents moist	60°	3 hrs.	40 cc
(3) Contents dry	60°	3 hrs.	15 cc
(4) Contents dry	60°	3 hrs.	20 cc

The evolved gas was colorless, insoluble in water, and developed a brown color with air. This supports our theory that a part at least of the pressure was due to NO, which resulted from the reaction with moisture.

Further precautions for drying the constituents were taken as follows: An H tube was made of 4 mm tubing.

One end was blown into a small bulb, and the whole carefully dried. A little P_2O_5 was placed in the bulb and covered with equal volumes of C_2Cl_4 and N_2O_4, previously dried over P_2O_5. The openings in the tube were then sealed and the liquid distilled to the second arm by gently heating the bulb, and freezing the second arm with CO_2 snow and ether. The connecting arm was then sealed, and the tube heated to 60° for three hours. It was cooled, opened, and the gases collected over mercury. About 3–5 cc of an inactive gas was evolved. This indicates that careful drying will eliminate the high pressure caused by the side reactions noted above. There remains then only the pressure of N_2O_4 to account for. Its vapor pressure at various temperatures are given in Table III.[1]

TABLE III

Temperature °C	Pressure, atmospheres
54.2	4.10
70.1	7.3
79.7	10.1
87.1	13.0
101.4	20.5
110.8	27.2

Autoclave Material

Since no porcelain-lined autoclave was available at first, a run was made in a phosphor-bronze autoclave. Accordingly 175 g. N_2O_4 and 320 g. C_2Cl_4 were placed in a tall beaker within the autoclave and the whole heated to 80° for three hours. A yield of 195 g. was obtained, 40 percent of the theoretical. The interior of the autoclave was badly corroded and it seems probable that the low yield was due to the nitrogen peroxide reacting with the metal.

We next attempted to use Bakelite varnish as a protective coating, but even when carefully baked it was almost completely destroyed as soon as subjected to the N_2O_4 vapors.

[1] Zeit. phys. Chem., **81**, 308.

We then tried placing the mixture of C_2Cl_4 in a large bottle, the mouth of which was loosely covered with a beaker. The whole was surrounded with sand and a top layer of iron filings. This method had to be abandoned on account of a very considerable loss of product by diffusion through the sand surrounding the reaction bottle.

An attempt was next made to find a metal sufficiently unaffected by N_2O_4. Small pieces of nichrome, copper, and iron wire, and spirals of copper and iron oxide were placed in tubes with N_2O_5 and P_2O_5, and heated to 80° both in the liquid and the vapor for three hours at 80°. The copper and copper oxide were badly attacked, and so heavy a pressure was developed that an attempt to open the tubes resulted in their being reduced to fragments. No pressure was developed in the tubes with the nichrome, and the iron and iron oxide, The last two showed no evidence of being attacked, but the nichrome was badly pitted.

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Since iron is apparently unattacked by dry N_2O_4, the following series of tests were made to determine the resistance of various kinds of iron when heated in a mixture of C_2Cl_4 and N_2O_4 at 80° for three hours. The results are summarized in Table IV.

TABLE IV

Iron	Condition of	Pressure developed	Condition of metal
(1) Steel	Mixture dry	Slight	Unattacked
(2) Steel	Mixture moist	Very high	Completely destroyed
(3) Wrought iron	Mixture moist	Very high	Completely destroyed
(4) Cast iron	Mixture dry	High	Badly attacked
(5) Wrought iron	Mixture dry		Unaffected

From the above results it seemed probable that a heavy-walled wrought-iron autoclave would prove satisfactory. Accordingly several runs were made using such a container but the efficiency was never better than 50 percent. Even with the most careful drying, the moisture absorbed by the C_2Cl_4-N_2O_4 mixture was sufficient to cause the walls to be

badly attacked and hence to contaminate the product with iron. This autoclave was therefore abandoned.

Later a porcelain-lined autoclave was obtained; but it leaked and was not satisfactory. The maximum efficiency obtained in it was 65 percent; but it is believed that this could be increased very materially under more favorable conditions. In Table V are given the yields obtained in the later runs with the three autoclaves.

TABLE V

Autoclave	C_2Cl_4	N_2O_4	(Temperature 80°)		% Yield
			Time	Product	
Phosphor-bronze	300 g	150 g	3 hrs.	205 g	58%
Iron	320 g	300 g	6 hrs.	245 g	50%
Porcelain-lined	400 g	230 g	6 hrs.	410 g	65%

Effect of Catalysts

If the temperature at which the reaction takes place could be lowered by the use of a catalyst, the difficulty in regard to material of construction would probably disappear because nitrogen peroxide makes iron passive at ordinary temperatures.

Four sealed tubes, each containing an approximately equal amount of a mixture of dry perchlorethylene and N_2O_4, were prepared containing the catalysts noted below, and allowed to stand at room temperature for three days. The results are noted in Table VI.

TABLE VI

Catalyst	Amount produced
Purified Dorsey charcoal	Few white crystals
Powdered filtchar[1]	Few white crystals
$AlCl_3$	.....
$ZnCl_2$	.....

[1] A commercial charcoal.

In no case was the amount produced equal to more than 1 to 2 percent of the theoretical.

Three more tubes were prepared, each containing approximately equal amounts of N_2O_4 and C_2Cl_4, the first two with Dorsey charcoal and filtchar, respectively, and the last without catalyst. They were heated 2 hours at 60° with the results summarized in Table VII.

TABLE VII

Catalyst	Temp.	Time	Wt. $C_2Cl_4N_2O_4$	% Yield
Dorsey charcoal	60°	2 hrs.	5–6 g	9
Filtchar	60°	2 hrs.	4–5 g	9
No catalyst	60°	2 hrs.	6–7 g	6

It is evident from the above results that the efficiency is affected but little by these catalysts.

A column of dried Dorsey charcoal contained in a wide tube, sealed at one end, was covered with anhydrous C_2Cl_4. The tube was surrounded with water at 80°. A reservoir, containing 150 cc of pure N_2O_4, was connected through a trap with a tube reaching to the bottom of the Dorsey column. The latter was provided with a reflux spiral condenser cooled with tap-water. The spiral was connected with another spiral condenser, cooled with water at 5° C, which returned the N_2O_4 liquid to the bottom of the reservoir. A bulb, containing P_2O_5 and open to the air, was sealed into the line immediately below the second condenser. By this means a continuous and rapid flow of gas was passed through the hot C_2Cl_4, and acted as an efficient stirring device for the catalyst. The run was continued for six hours, the apparatus disconnected, and the C_2Cl_4 and Dorsey charcoal separated. The volume of the liquid had increased, rising over 1 cm in the tube. Evaporation yielded 3–4 g of the product, 3 percent of the theoretical.

Although much N_2O_4 was lost through difficulties encountered in keeping the second condenser at a sufficiently low temperature, it seems evident that, even with perfect

condensation of the peroxide, this method is impracticable since so long a run would be necessary to produce a noticeable amount of the compound.

It will be observed from the above experiment and others which have preceded it, that the reaction

$$C_2Cl_4 + N_2O_4 \longrightarrow C_2Cl_4N_2O_4$$

only proceeds smoothly under the following conditions:

(1) Temperature of 80°.

(2) Heating 3–6 hours.

(3) Pressure about 10–12 atmos. (See Table III, V. P. of N_2O_4.)

(4) Excess of *liquid* N_2O_4.

The last point indicates, as does the experiment just described, that the reaction takes place mainly in the liquid and not in the gaseous phase, and in consequence the most favorable conditions would be a small gas space, and an excess of N_2O_4, conditions which we were unable to produce in our autoclave on account of the difficulty of obtaining sufficiently large amounts of dry N_2O_4.

Solubility

It was found that 30 cc of dry N_2O_4, distilled from P_2O_5, will dissolve 15.7 g. of $C_2Cl_4(NO_2)_2$ at 0°. The solubility in superpalite and chorpicrin was not determined quantitatively but seemed to be of the same order.

Owing to the signing of the armistice, further work on the preparation and properties of tetrachlordinitroethane was discontinued. This work was begun while the Catalytic Laboratory was under the Bureau of Mines and was continued after the transfer to the War Department. It was carried out under the general supervision of W. D. Bancroft.